

Quantum chemistry for surface segregation in metal alloys (DE-FG26-05NT42539)

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Hydrogen Permeable Membranes

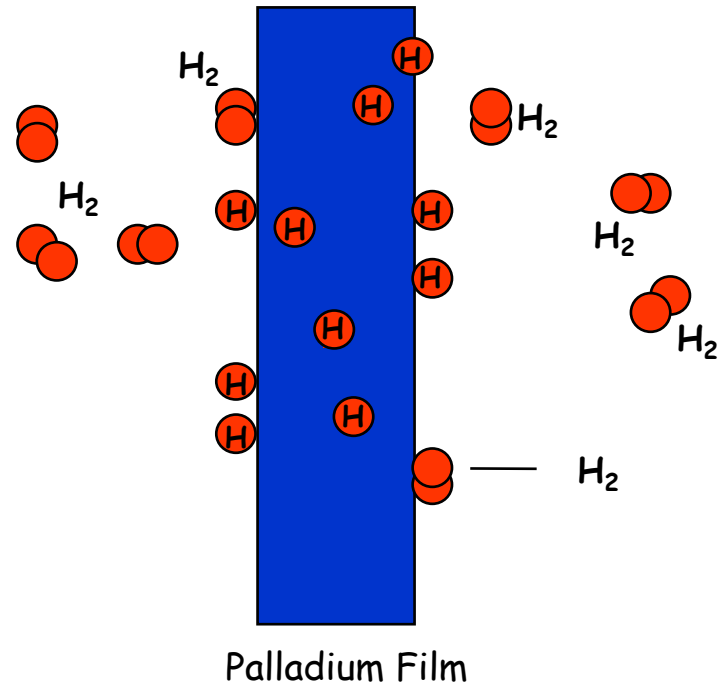
- ❖ Highly selective hydrogen permeable membranes are vital in large-scale H_2 separation and purification processes

Problems with Traditional Pd membranes

- ❖ Poisoning by non-hydrogen species (Sulfur)
- ❖ Hydrogen embrittlement

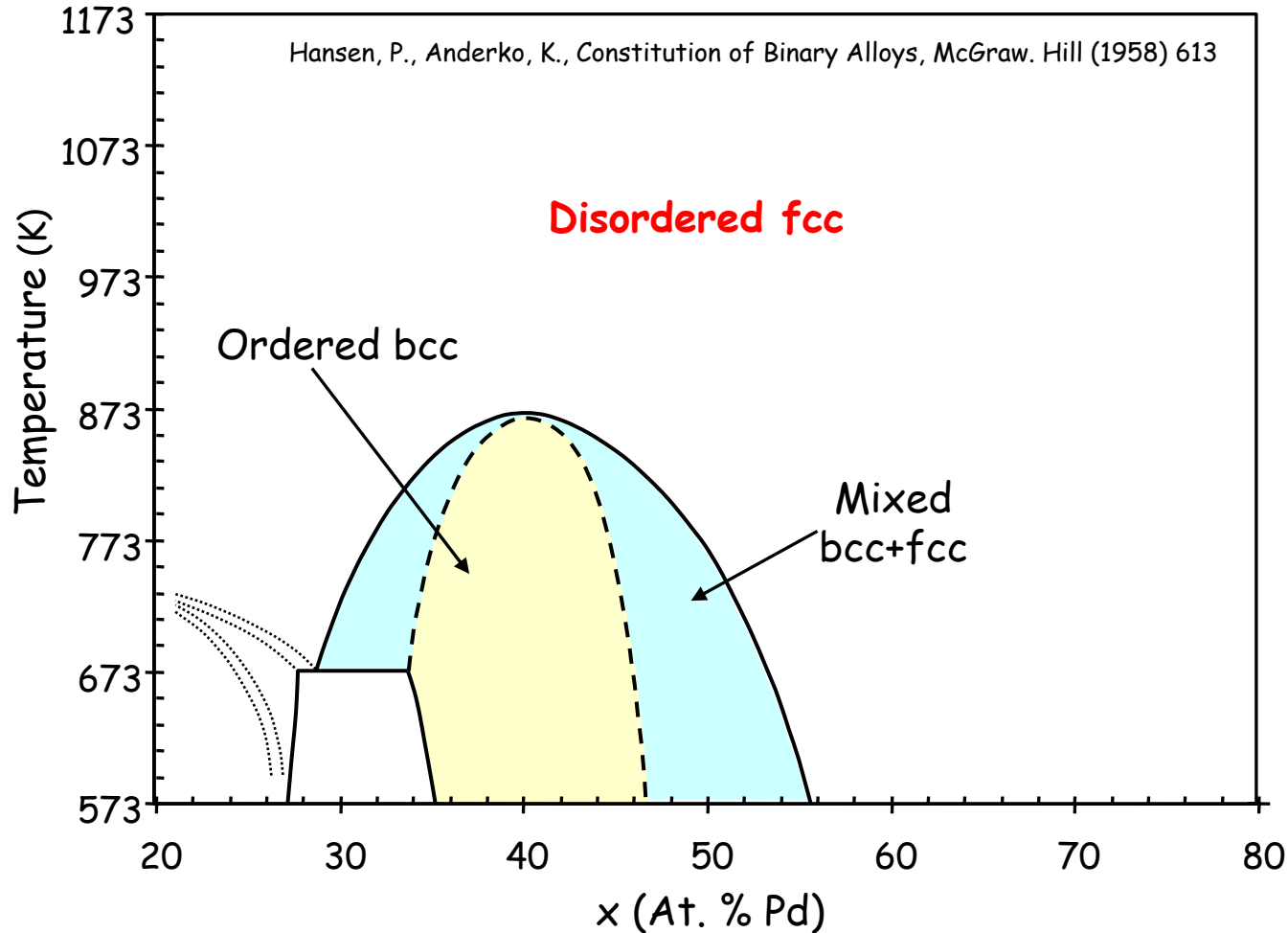
Criteria for choosing alloy membranes

- ❖ High flux (Solubility, Diffusivity)
- ❖ Thermal Stability
- ❖ Cost

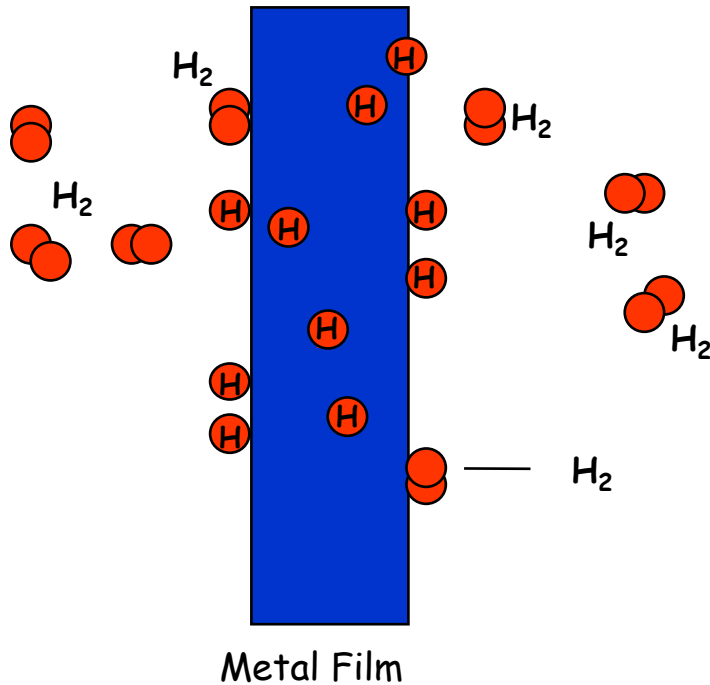


Bulk $\text{Cu}_{100-x}\text{Pd}_x$ Alloys

One set of binary alloys with useful properties as H_2 membranes are PdCu alloys



Bulk vs. Surface Properties



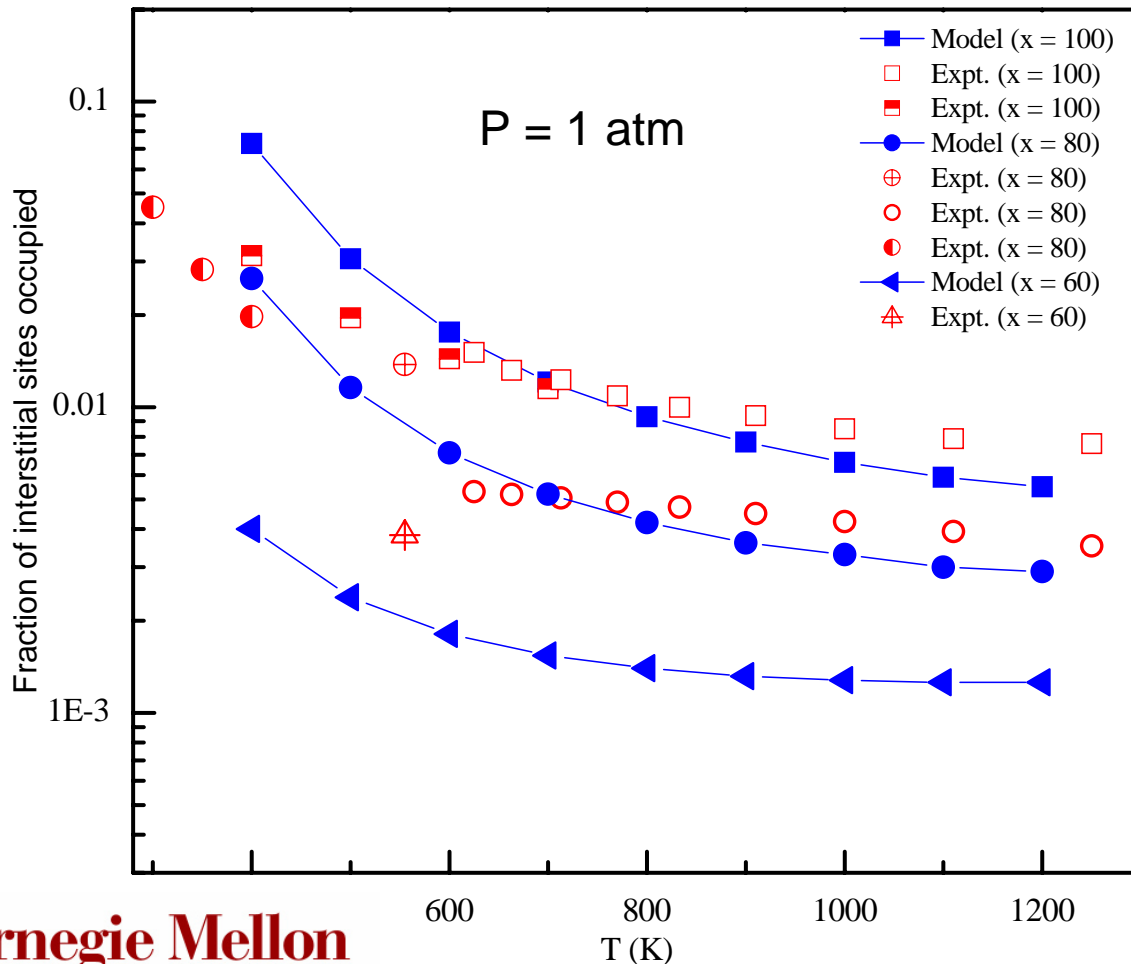
The overall performance of a metal membrane involves both surface and bulk properties.

Except perhaps for ultra-thin films, the net permeance is controlled by a combination of H solubility and H diffusion in the bulk material. These properties are well suited for treatment using quantum chemistry methods.

Prediction of H Solubility

Kamakoti et al., Science, **307** (2005) 569

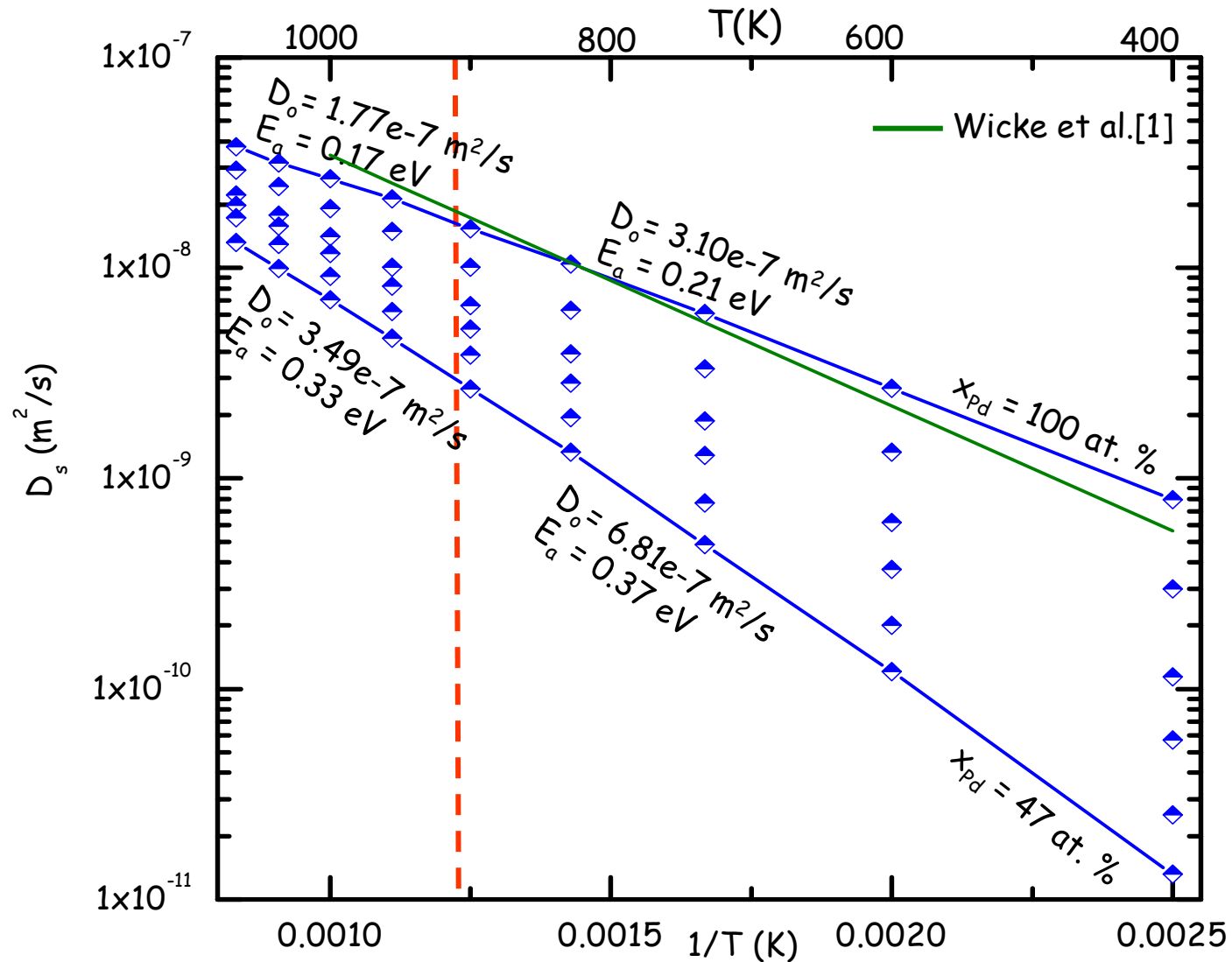
- ❖ Plane wave DFT calculations for H energy in individual interstitial sites
- ❖ Statistical mechanical model to predict Sievert's constants and H solubility



Concentration of interstitial H is dilute over a wide range of conditions

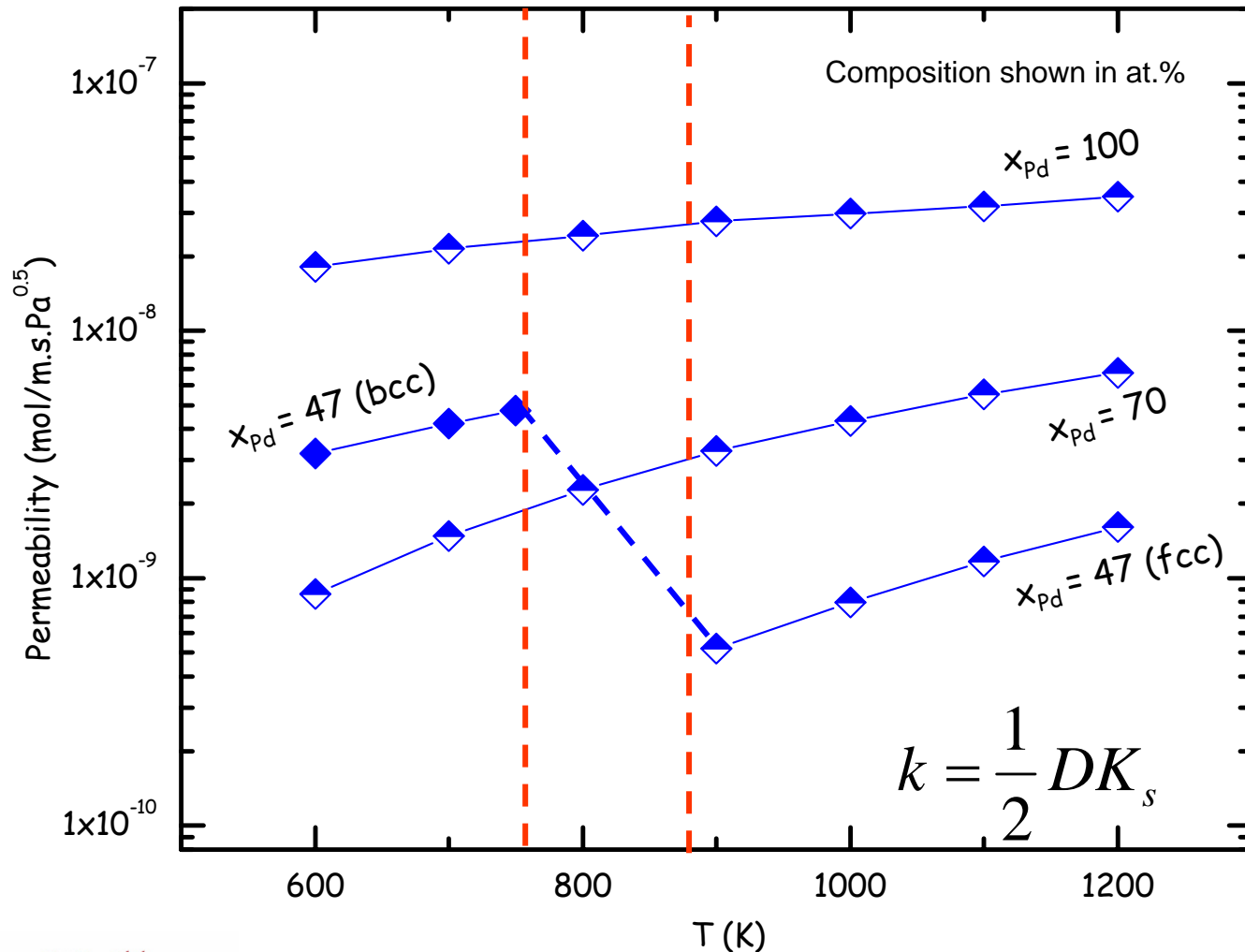
Prediction of H Diffusivities in Fcc CuPd

Kamakoti, P., Sholl, D.S., Phys. Rev. B **71** (2005) 014301



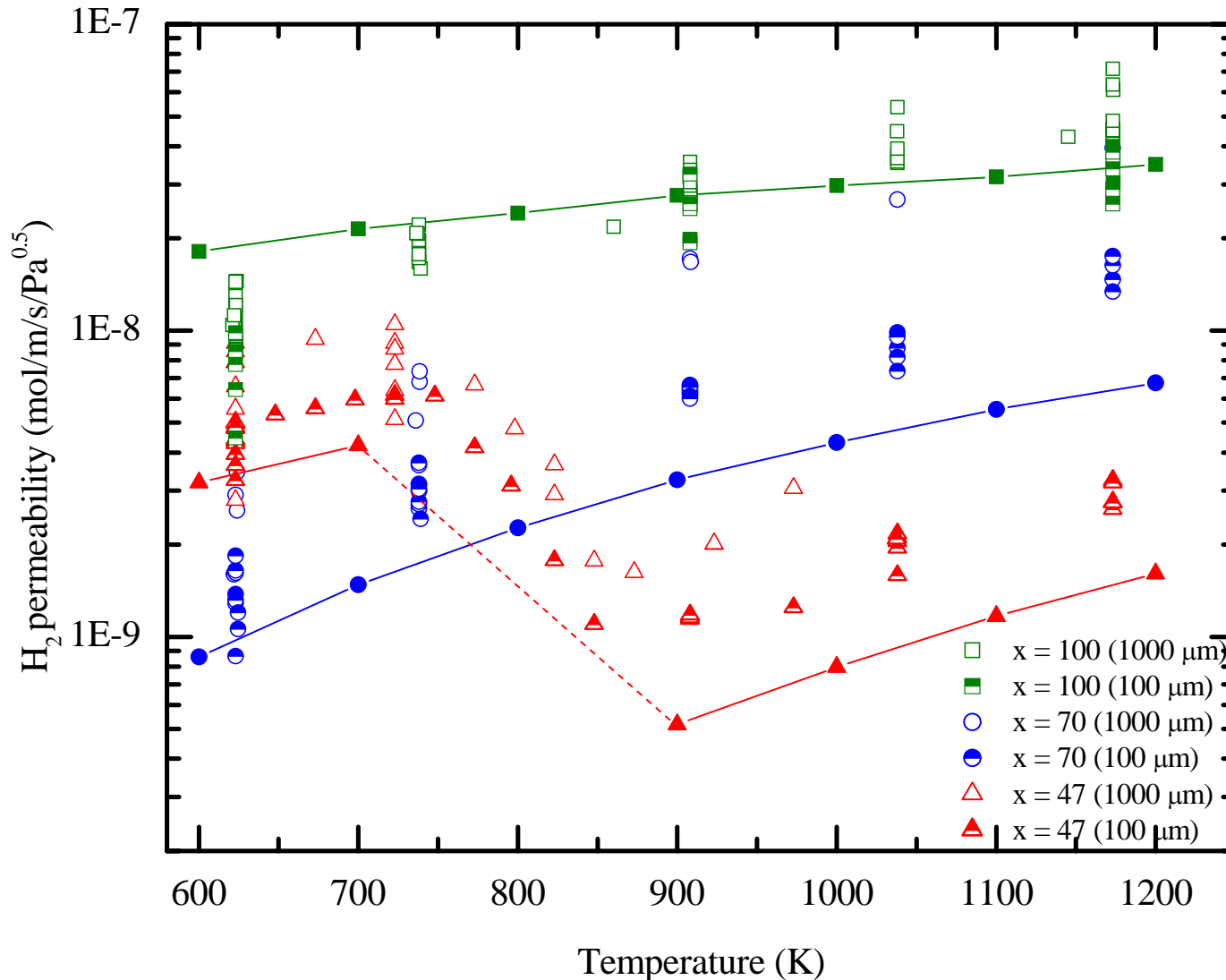
Predicted Membrane Properties

Our DFT-based approach predicts membrane properties with no experimental input



Membrane Properties: Model vs. Expt.

Kamakoti et al., Science, **307** (2005) 569



All experiments performed at NETL under steady state conditions

Our DFT-based approach makes quantitative predictions with no experimental input

Computational Screening of Ternary Alloys

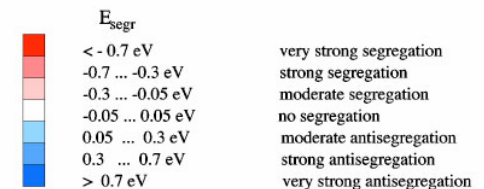
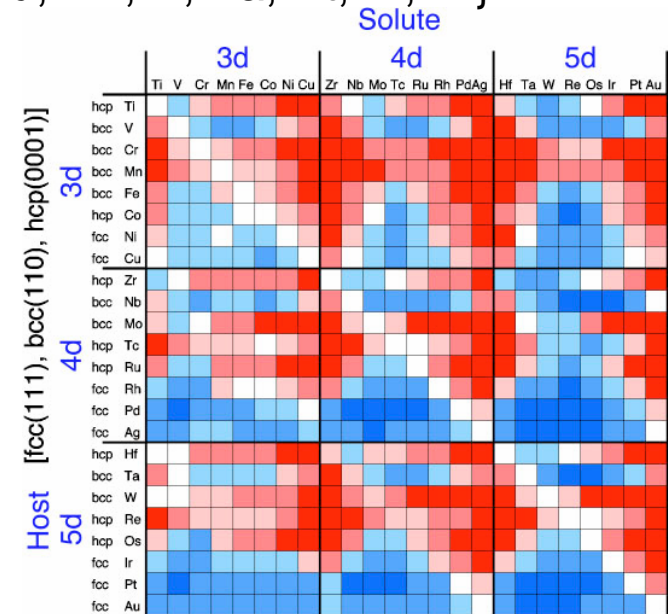
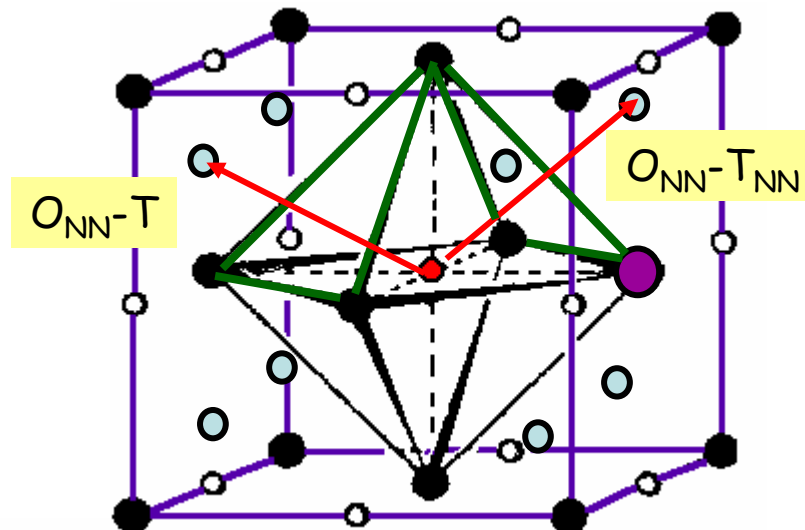
Kamakoti & Sholl, J. Membrane Sci., in press

These quantum chemistry based methods have been extended to screen potential ternary alloys based on PdCu binary alloys

Initial efforts focus on $\text{Pd}_{74}\text{Cu}_{22}\text{M}_4$ with $\text{M} = \{\text{Zn}, \text{Ru}, \text{Rh}, \text{V}, \text{Ta}, \text{Pt}, \text{Ti}, \text{Zr}\}$

M chosen to exclude surface segregation in Pd and Cu using *ab-initio* database of Ruban *et al.* Phys. Rev. B **59** (1999) 15990

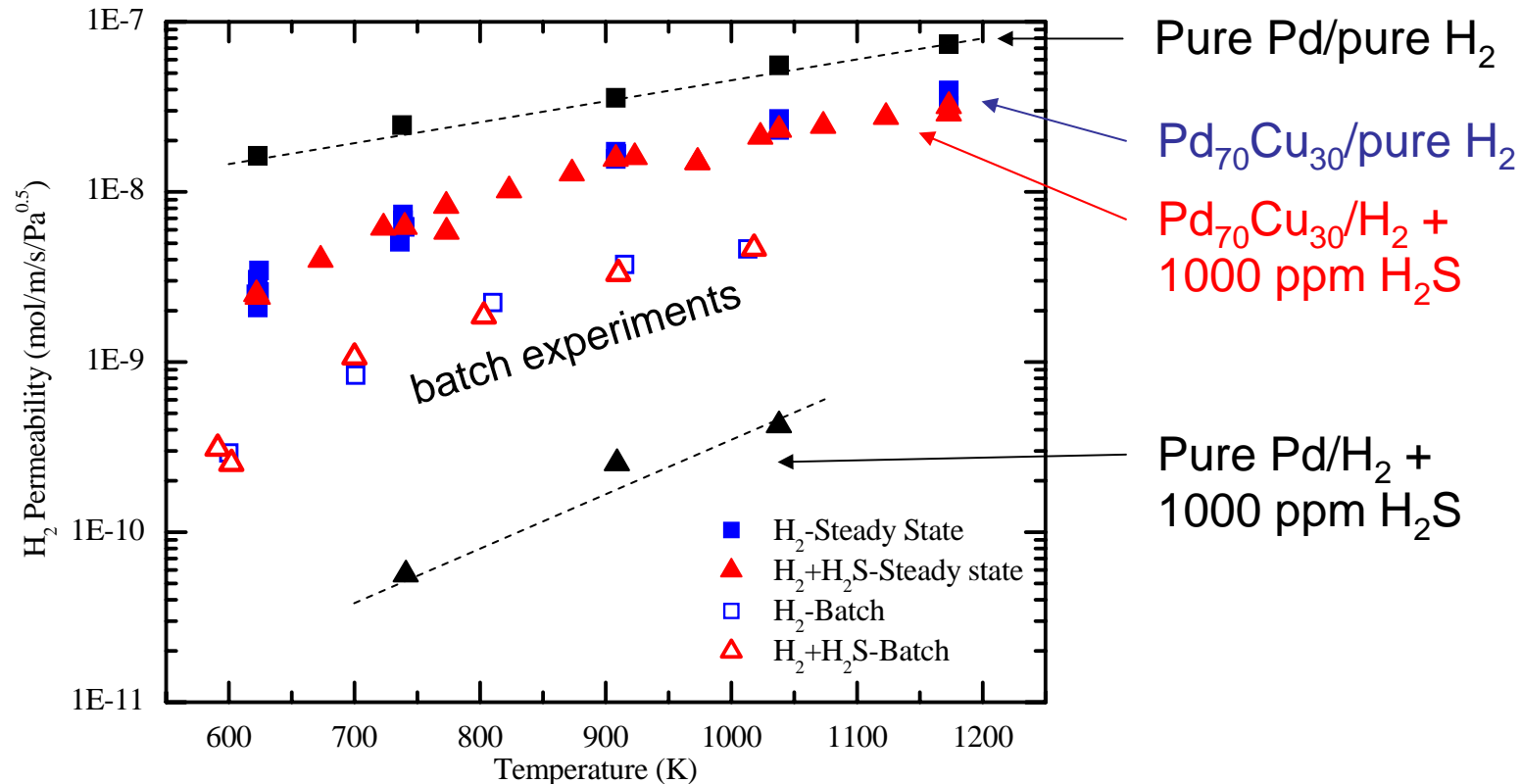
M treated as random substituent in fcc lattice



Surface Properties Are Also Crucial

Kamakoti et al., Science, **307** (2005) 569

How do the membranes perform in the presence of H_2S ?



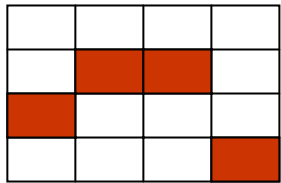
What is the mechanism of S resistance??

Understanding the surface structure is a prerequisite to answer this question.

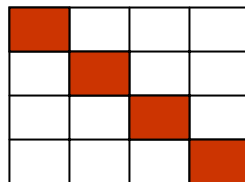
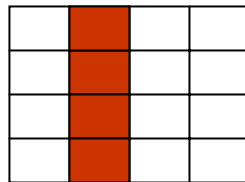
Order/Disorder in Single Surface Layers

Each layer of a surface alloy can have many possible two dimensional orderings of atoms.

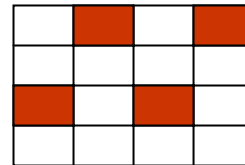
Example: Two-dimensional square lattice with 75/25 composition



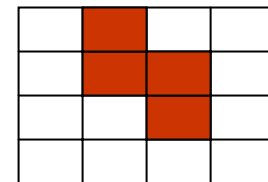
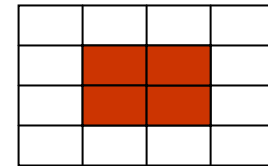
random structure
(one of many)



“striped” phases



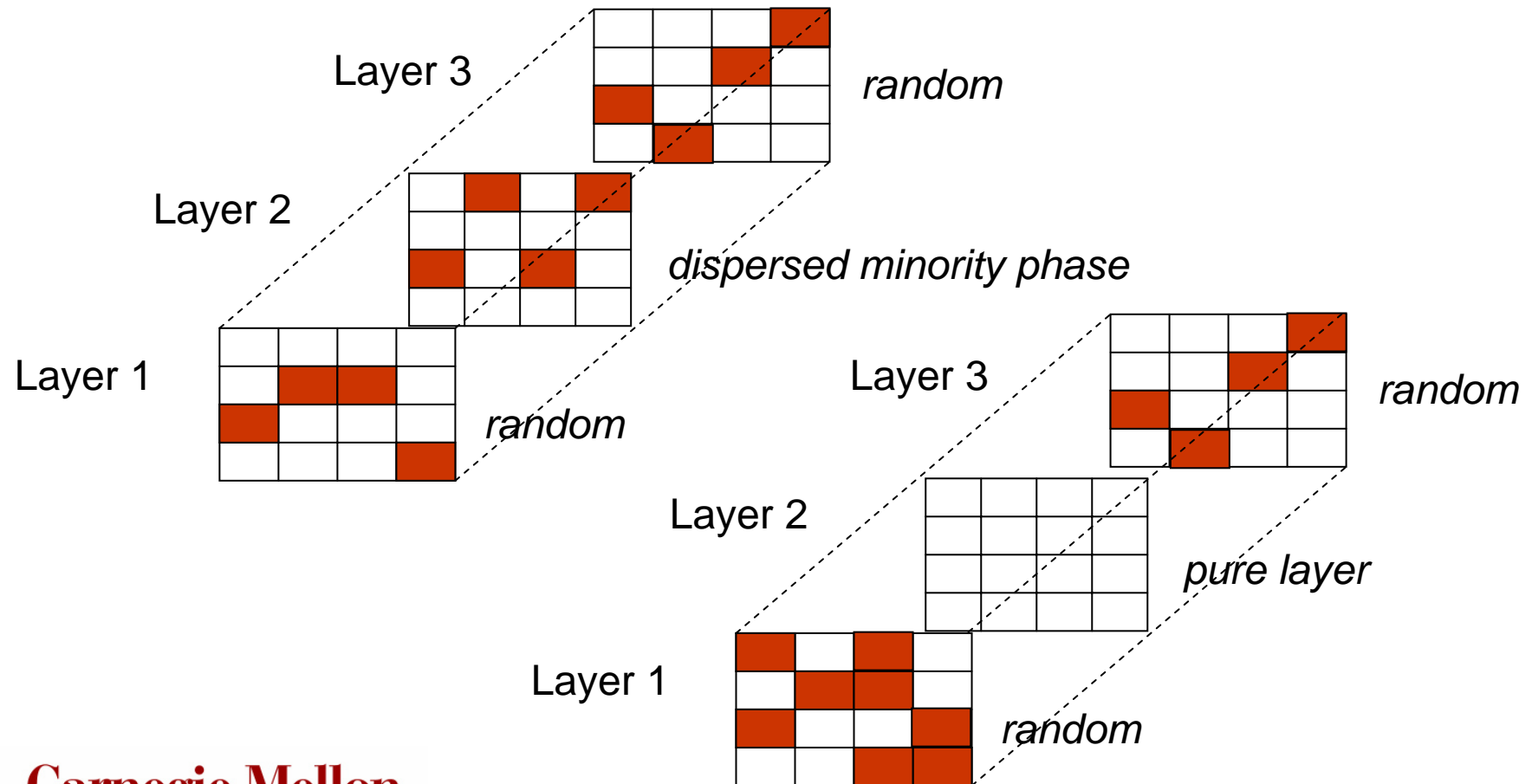
well dispersed
minority species



clustered minority
species

Order/Disorder in Multiple Surface Layers

When multiple alloy layers are present, each layer can exhibit multiple structures and varying composition (surface segregation)



Objective



Our aim is to use rigorous first-principles methods to predict the strength of surface segregation in binary alloys relevant for H₂ purification membranes.

Considerable previous theoretical work has been done, but none that is suitable for this particular application

First principles methods have been applied to “dilute” alloys (i.e. one substituent atom in the surface of an otherwise pure element) (e.g. Ruban et al. Phys. Rev. B 59 (1999) 15990)

Extensive calculations with semi-empirical potentials (e.g. Embedded Atom method). These calculations cannot be extended to adsorbate-covered surfaces without complete reparameterization of the interatomic potential.

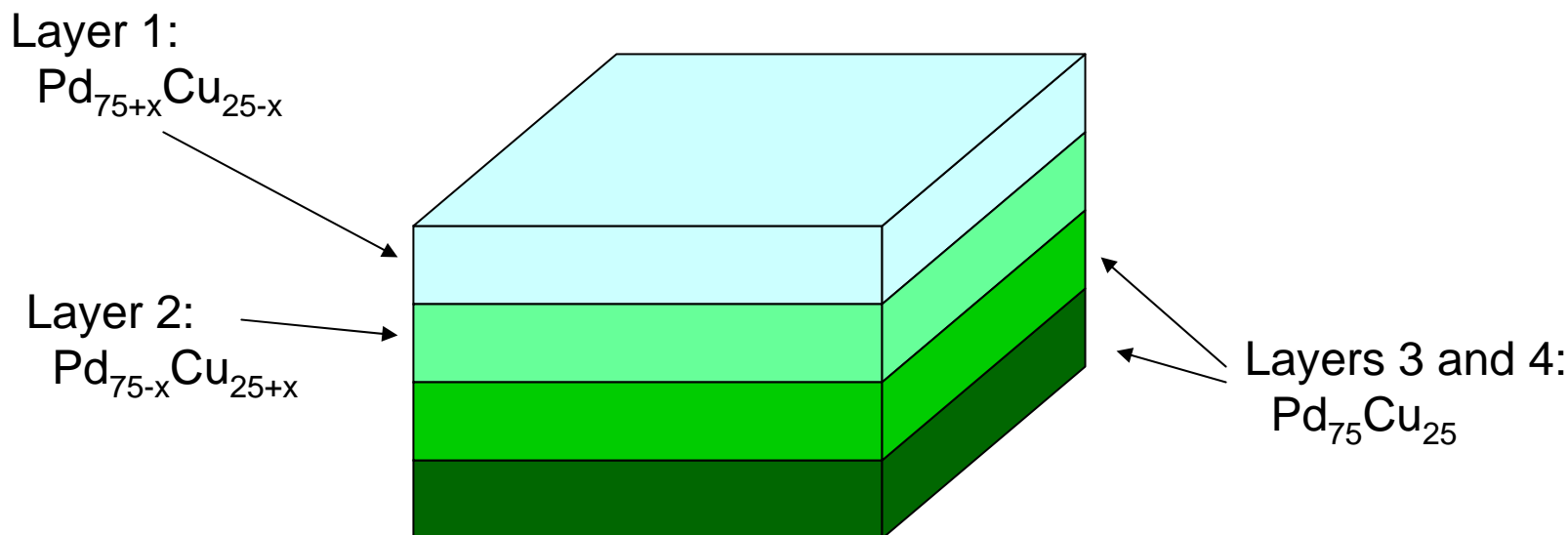
First principles methods have been widely applied to “near surface alloys” but almost always without concern for the overall thermodynamic stability of the surface phases (e.g. Greeley and Mavrikakis, Nature Materials 3 (2004) 810)

Surface segregation is important in other technologically relevant contexts (e.g. bimetallic catalysts), so robust methods will have wide application.

Theoretical methods will complement experimental approaches (e.g. low energy ion scattering) that are well known but have not been widely used.

DFT Calculations for $\text{Pd}_{75}\text{Cu}_{25}(111)$ Surfaces

All calculations performed for 4-layer slab of fcc $\text{Pd}_{75}\text{Cu}_{25}(111)$ allowing redistribution of Cu between layers 1 and 2 (but not with bulk layers)

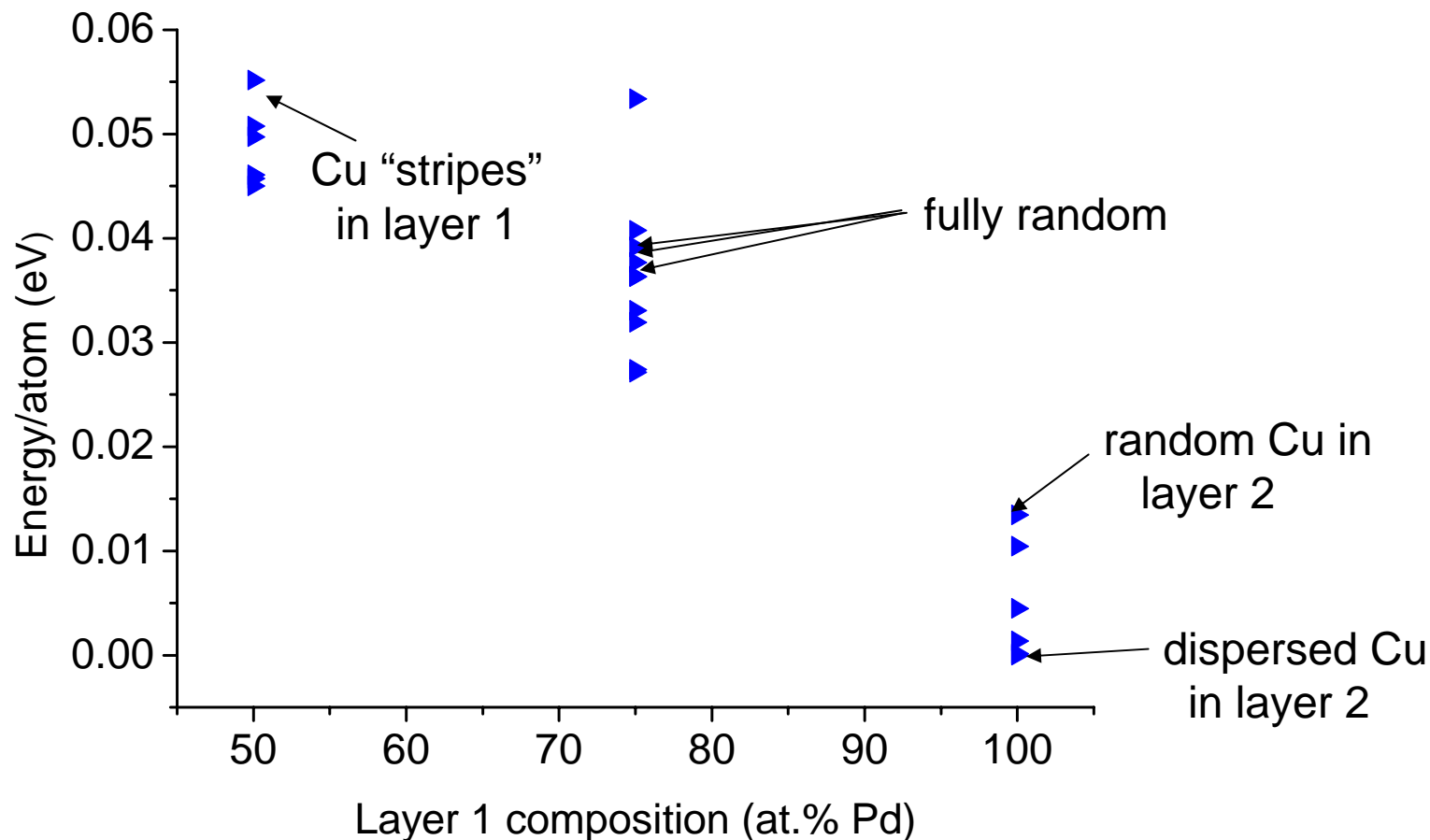


- Lattice constant fixed by DFT-computed result for bulk material
- Atoms in layers 3 and 4 fixed in bulk-truncated positions, but full relaxation in layers 1 and 2.
- GGA-PW91 calculations performed with VASP using $1 \times 1 \times 1$ k -point.
- Test calculations with higher resolution in k -space $1 \times 1 \times 1$ results are acceptable
- All calculations used a (4×4) surface unit cell

For several possible layer compositions, a “library” of structures was examined to probe effect of order/disorder within layers.

DFT Energies for Pd₇₅Cu₂₅(111) Surfaces

Energies shown per atom in two active layers (32 active atoms in supercell)



This data strongly points to Cu anti-segregation from surface, but it is difficult to draw quantitative conclusions from this data alone.

Cluster Expansions for Alloy Properties

(S. Muller, J. Phys. Condens. Matter 15 (2003) R1429)

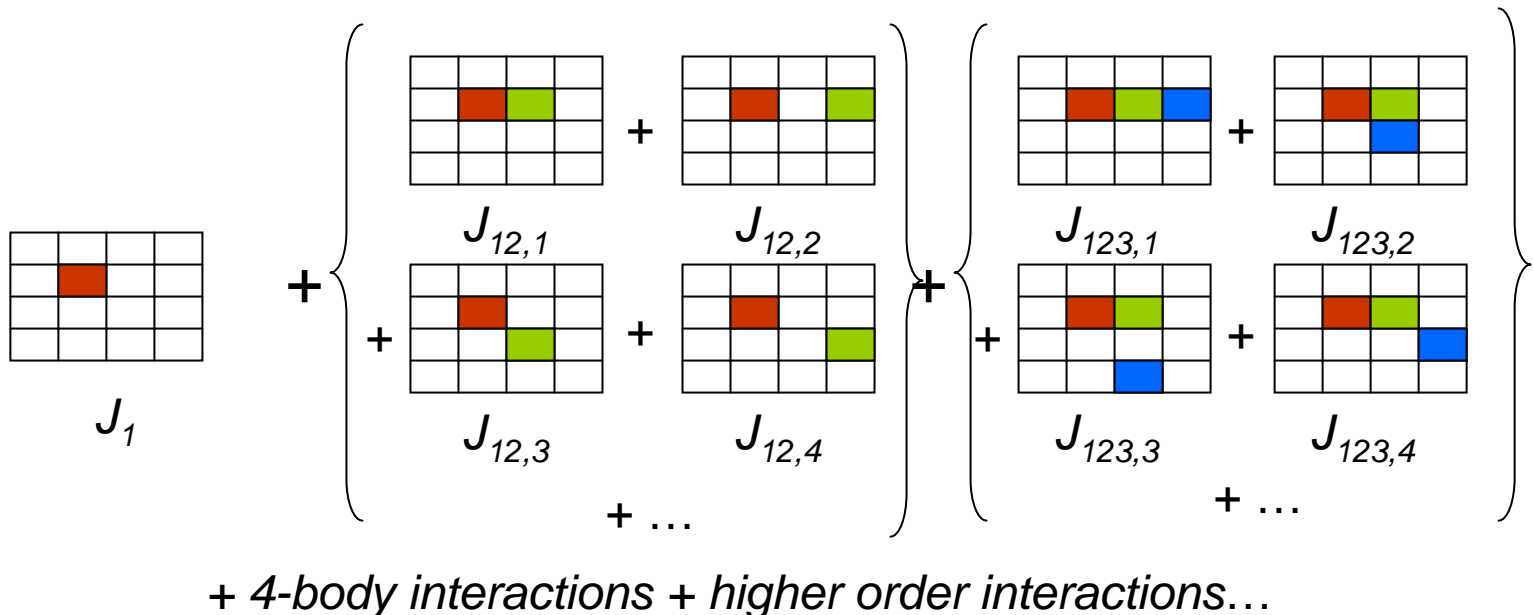
Total energy of arbitrary arrangement of atoms within crystal structure can formally be represented as a cluster expansion.

The illustration here uses a two-dimensional square lattice for clarity.

E = site energies

+ pair interactions

+ 3-body interactions

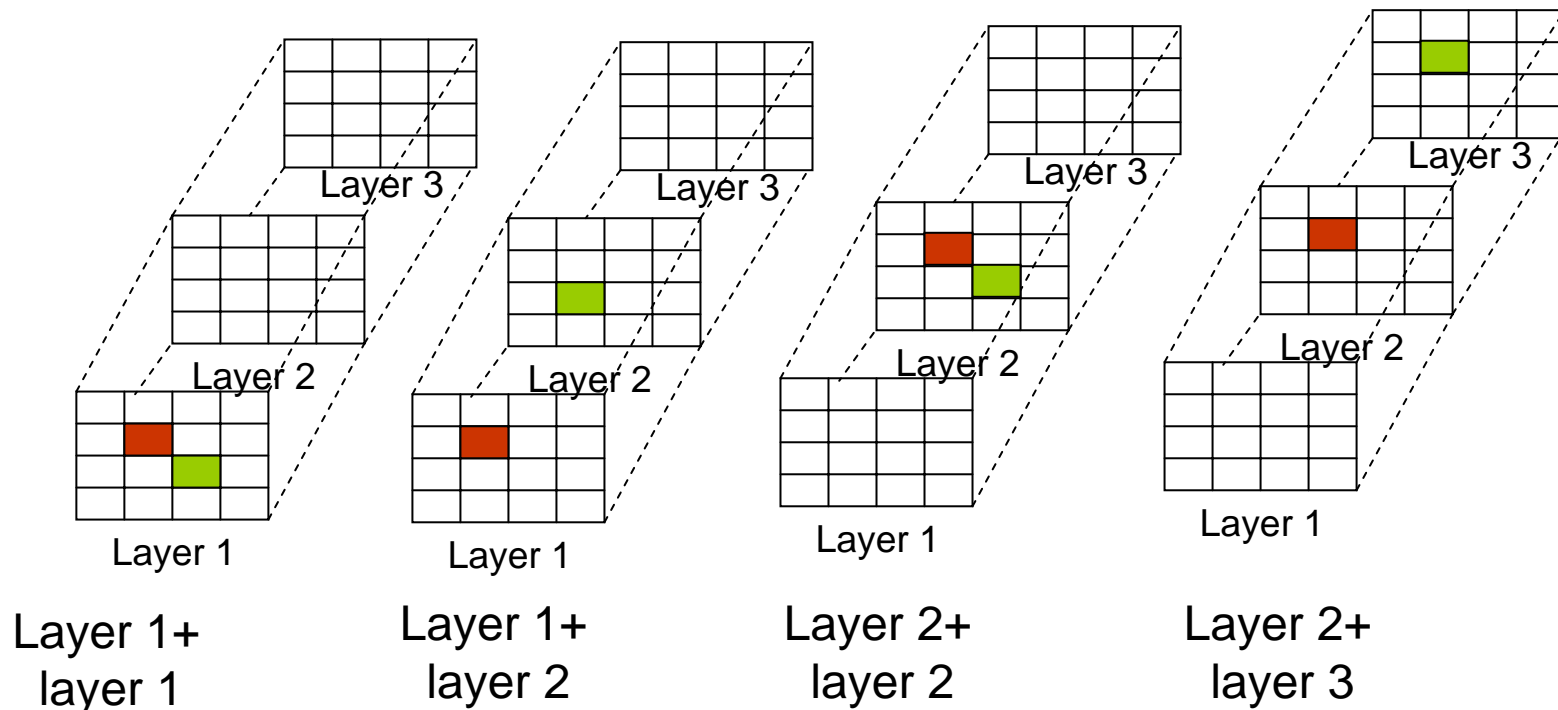


To use this approach, the infinite set of interaction parameters must be truncated and the values of the retained parameters must be determined.

Cluster Expansions for Surface Properties

Cluster expansion must distinguish between surface layers

Potential two body interactions include:



Statistically Significant Interactions - LOO Method

Many possible truncations of cluster expansions exist. How can the collection of statistically significant interactions be readily determined?

Consider a model with up to m interaction parameters. We aim to compare this to all models with $(m-1)$ parameters, $(m-2)$ parameters etc. as fits to a data set with N total total energies.

For model with m parameters, define J_k = least squares solution for interaction parameters using all data except the k -th energy (“leaving one out”).

Then define the “leave one out error”

$$R_{loo}^2 = \frac{1}{N} \sum_{k=1}^N [E(J_k) - E_k]^2$$

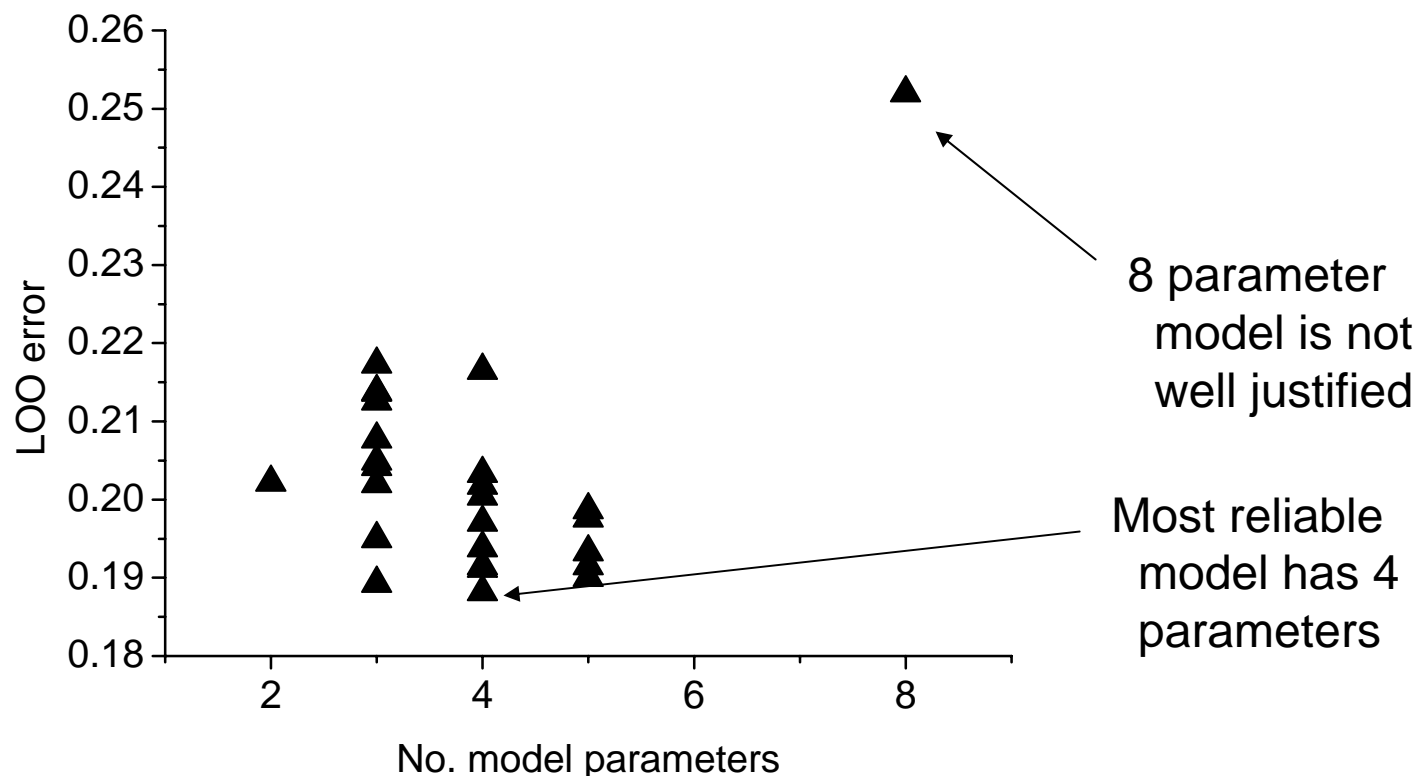
model prediction observed energy

From the set of all possible models, the model that minimizes the leave one out error is the most statistically reliable.

The final model is the least squares solution of the chosen model using *all* data.

LOO Results for $\text{Pd}_{75}\text{Cu}_{25}(111)$

Truncated cluster expansions compared using full DFT data set shown earlier



4 parameter model has two parameters controlling overall layer composition, one parameter defining local ordering in layer 1, and a final parameter defining local ordering in NN atoms in layers 2 and 3.

Kinetic Monte Carlo Simulation of Lattice Model



Once a truncated cluster expansion has been selected, the equilibrium states of the system can readily be assessed using Kinetic Monte Carlo (KMC).

For a binary alloy, KMC moves involve computing the energy change associated with switching the atoms in two arbitrary lattice sites, ΔE . Attempted moves are accepted according the Metropolis criterion:

If $\Delta E < 0$, always accept move

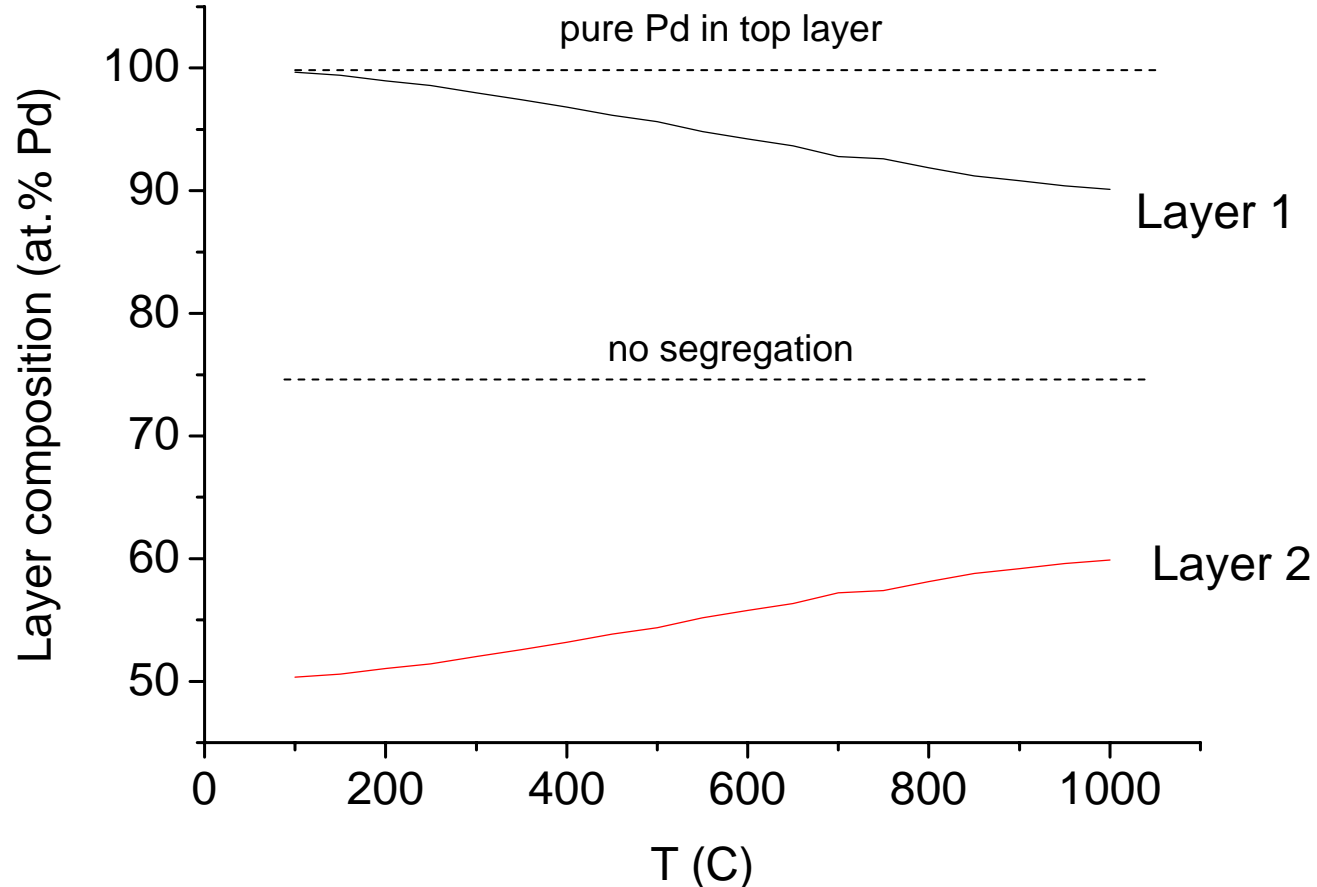
If $\Delta E > 0$, accept move with probability $\exp(-\Delta E/kT)$

To be consistent with our DFT calculations, KMC only performed for systems in which the total Cu content of the top two layers was fixed but Cu was allowed to exchange position with Pd among these two layers.

KMC simulations performed using 10×10 atoms in each surface layer, with 2×10^5 KMC moves for data collection after equilibration with 10^5 moves from initially random structure. Test calculations with much larger systems used to verify that these choices yield well converged results.

KMC Results

Principal outcome from KMC is the equilibrium composition of the top two layers as a function of temperature



Our calculations predict strong segregation of Pd to the surface. At the high temperatures relevant for membrane operation, top layer is 90-100% Pd.

H Binding Energies on Equilibrium Surfaces



One implication of surface segregation is that binding energies of chemical species on the equilibrium surfaces will differ from stoichiometric surfaces.

Previous DFT studies of H and S binding on fcc PdCu surfaces assumed the surface structure was stoichiometric (e.g. Alfonso, Cugini, and Sholl, Surf. Sci. 546 (2003) 12)

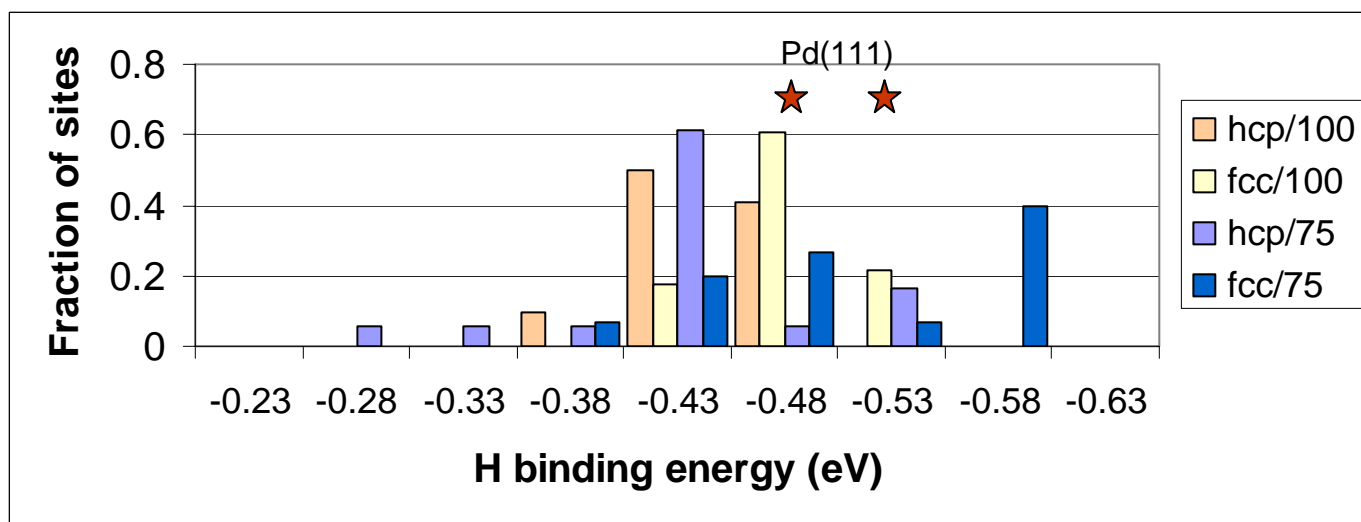
On disordered surfaces, a range of binding energies exist because of changes in local atomic environment. Results for a representative sample of sites are needed to draw physical conclusions.

The binding energy of atomic H is a useful probe of surface chemisorption (and is highly relevant to practical membrane operation). H binding energies control the H coverage on membrane surfaces and also the possibility that surface effects contribute to deviations from “simple” relationship between pressure drop and permeance (Ward and Dao, J. Membrane Sci. 153 (1999) 211)

H Binding Energies on Equilibrium Surfaces (cont.)

GGA-PW91 calculations performed for H adsorption in 3-fold sites on surfaces with 100 or 75 at.% Pd in top layer (2x2x1 k-points, (4x4) surface unit cell, 4 layer slab)

Binding energy defined as energy change for $\frac{1}{2} \text{H}_{2(g)} \rightarrow \text{H}_{(a)}$ (without zero point energies)

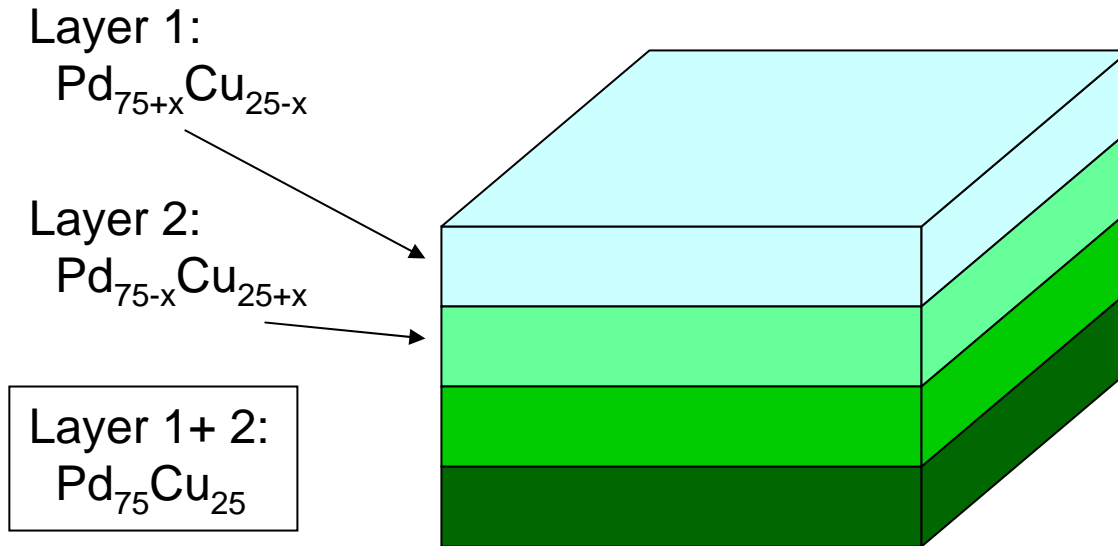


On both surfaces, fcc sites favored over hcp sites (on average).
Surface segregation of Pd reduces spread of H binding energies and reduces average binding energy relative to stoichiometric surface

Similar trends are likely for S adsorption (although no data currently available)

Limitations of Our Current Results

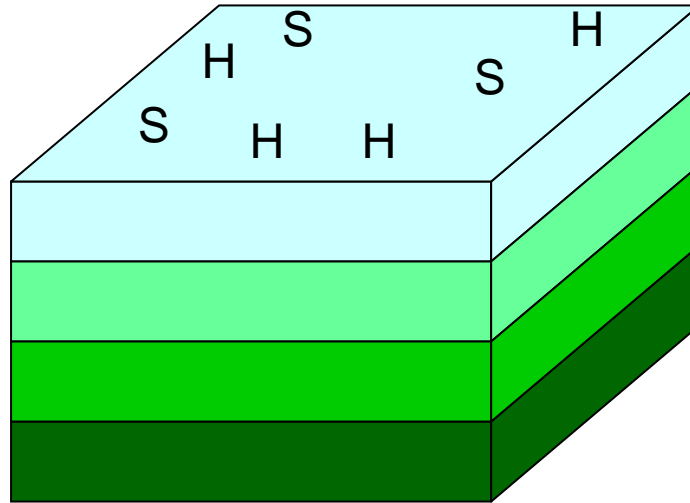
Our results are based on allowing mass redistribution only between top 2 layers



In reality, the net composition of the top 2 layers may differ from the bulk composition. This possibility can be described within the current approach by using an expanded library of DFT calculations and relating slabs of differing net composition via the chemical potential of each constituent computed for a bulk sample.

Limitations of Our Current Results (cont.)

Our predicted surface compositions are for bare surfaces in vacuum.
What will change in the presence of strongly adsorbing species (e.g. S)?



Detailed calculations are possible for specific examples, but developing a comprehensive picture would be time consuming.

Since S bind more strongly to Pd than Cu (see, e.g., Alfonso et al. Surf. Sci 546 (2003) 12), we speculate that S adsorption will tend to increase Pd segregation. Because predicted segregation on bare surface is already strong, adsorbed S will have at most a small effect on the equilibrium surface composition.

Conclusions and Future Directions



The use of DFT + cluster expansions + KMC is a useful approach to describe equilibrium surface segregation in alloy surfaces. Information from this approach can complement experimental approaches using Low Energy Ion Scattering.

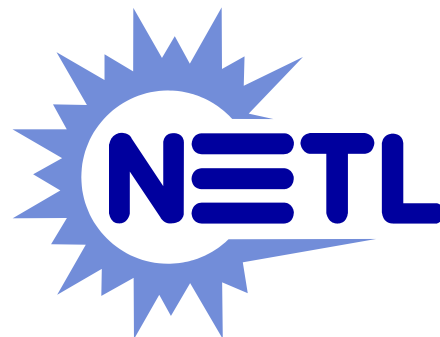
The example we have studied is a binary alloy relevant for H₂ purification membranes, but many other technologically important uses of alloy surfaces also exist (e.g. bimetallic catalysts).

For Pd₇₅Cu₂₅(111) in vacuum, our calculations predict considerable segregation of Pd into the top surface layer. For $T < 1000$ °C, the top layer is predicted to be > 90 at.% Pd

As in applications to bulk alloys, a more general use of the cluster expansion approach is to use it to identify additional configurations to be added to the DFT library to improve overall accuracy (S. Muller, J. Phys. Condens. Matter 15 (2003) R1429)

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